

Thermodynamic reference model for elastic-plastic solids undergoing phase transformations (*)

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A THERMODYNAMICAL framework for modeling the behaviour of elastic-plastic metallic solids under an ongoing phase transformation is provided. The material element is treated as multiphase multicomponent system being in constrained equilibrium. Its internal state is described by a set of intrinsic inelastic strains, weight fractions of all phases and parameters representing their chemical composition. The simple relation between total overall strain and intrinsic elastic strain is adopted, and each individual phase is regarded as an open elastic-ideal plastic subsystem. It is shown that transformation-induced intrinsic plasticity and strain-induced transformations can be regarded as thermodynamic cross-effects. The specific free energy of multicomponent single phase solid is derived using the observation that specific heat at fixed strain above the Debye temperature is sensibly constant for most metallic solids. The ideal metallic element considered here reduces to a mixture of „ideal solid solutions” in the limit when strain effects are neglected. The effect of initial extra stresses due to phase formation on transformation-induced total strain is discussed.

Zbudowano ogólne ramy termodynamicznej teorii ciał sprężystoplastycznych ulegających przemianom w stanie stałym. Element materialny traktowany jest jako wielofazowy wieloskładnikowy układ termodynamiczny znajdujący się w stanie zahamowanej równowagi w każdej chwili procesu. Jego stan termodynamiczny opisany jest przez zbiór wewnętrznych niesprężystych odkształceń plastycznych faz, zbiór udziałów wagowych faz oraz zbiór parametrów reprezentujących chwilowy skład chemiczny poszczególnych faz. Przyjęto prosty związek pomiędzy całkowitym globalnym odkształceniem makroelementu i wewnętrznymi odkształceniami sprężystymi faz. Fazy traktuje się jako jednorodne otwarte podukłady sprężysto-idealnie plastyczne. Pokazano, że tzw. plastyczność przemian fazowych oraz odkształceniowe przemiany fazowe można traktować jako termodynamiczne efekty krzyżowe. Wykorzystując wnioski płynące z klasycznej teorii Debye'a podano częściowo wyspecyfikowaną postać funkcji energii swobodnej ciała wielofazowego. Rozważany tu układ termodynamiczny redukuje się do mieszaniny tzw. „idealnych roztworów stałych” w granicy, gdy efekty naprężeń ścinających są pominięte. W pracy przedyskutowano także wpływ różnicy początkowych naprężeń wewnętrznych (naprężeń uśrednionych po obszarach poszczególnych faz) na zjawisko plastyczności przemian fazowych.

Построены общие рамки термодинамической теории упруго-пластических тел, подлежащих фазовым превращениям в твердом состоянии. Материальный элемент трактуется как многофазную многокомпонентную термодинамическую систему, находящуюся в состоянии заторможенного равновесия в каждый момент процесса. Ее термодинамическое состояние описывается множеством внутренних неупругих пластических деформаций фаз, множеством весовых частей фаз, а также множеством параметров, представляющих мгновенный химический состав отдельных фаз. Принято простое соотношение между полной глобальной деформацией макроэлемента и внутренними упругими деформациями фаз. Фазы трактуются как однородные открытые упруго-идеально пластические подсистемы. Показано, что т.наз. пластичность фазовых превращений и дефор-

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мационные фазовые превращения можно трактовать как термодинамические перекрестные эффекты. Используя следствия вытекающие из классической теории Дебая, приведен частично специфицированный вид функции свободной энергии многофазного тела. Рассматриваемая здесь термодинамическая система сводится к смеси т.наз. „идеальных твердых растворов” в пределе, когда пренебрегается эффектами напряжений сдвига. В работе обсуждено также влияние разницы начальных внутренних напряжений (напряжений усредненных по областях фаз) на явление пластичности и фазовых превращений.

List of most important symbols

- $M, M_K, M^\alpha, M_K^\alpha$ fixed total mass of macroelement, mass of component K , mass of phase α and mass of component K in phase α ,
- V, V^α volume of macroelement and volume of a phase α ,
- ρ, ρ^α mean mass densities of the macroelement and the phase α ,
- $c^\alpha, v^\alpha, x_K^\alpha$ mass and volume fractions of the phase α , and mass fraction of the component K in the phase α ,
- n, r number of phases and number of components,
- Φ^α, S^α total free energy and total entropy of single-phase macro-element (phase α),
- E_α^e thermodynamic elastic strain tensor of homogeneous single-phase element (phase α),
- T, T_0 thermodynamic temperature and reference temperature,
- $\bar{\tau}_\alpha, \bar{\sigma}_\alpha$ Kirchoff and Cauchy's stress tensors of homogeneous single-phase element,
- $\mu_K^\alpha, \bar{\mu}_K^\alpha$ common and generalized chemical potentials of the component K in the phase α ,
- $u_\infty^*, s_\infty^*, s_1^*$ specific internal energy and specific entropy of the phase α at natural state, and entropy of mixing of single-phase α ,
- ϕ, u, s overall specific free energy, internal energy and entropy of multiphase multicomponent element,
- c_v, c_v^α specific heats: overall and of the phase α at constant elastic strain,
- L, L_α isothermal elastic stiffnesses: overall and of the phase α ,
- L^0, L_α^0 isothermal elastic stiffnesses at $T = T_0$,
- \bar{L}, \bar{L}_α elastic thermal softening: overall and of the phase α ,
- M, M_α isothermal elastic compliances: overall and of the phase α ,
- β, β^0 tensor of overall elastic thermal stresses and its value at $\epsilon_\alpha^e = 0$,
- $\beta_\alpha, \beta_\alpha^0$ tensor of elastic thermal stresses of the phase α and its value at $\epsilon_\alpha^e = 0$,
- $\alpha_\alpha, \bar{\alpha}_\alpha$ tangent and secant (engineering) thermal expansion of the phase α ,
- $\alpha, \bar{\alpha}$ overall tangent and engineering thermal expansion,
- $\tau, \sigma, \tau_\alpha, \sigma_\alpha$ Kirchoff and Cauchy's stress tensors: overall and intrinsic in the phase α ,
- $\hat{\rho}, \hat{\phi}, \hat{s}, E, T$ local fields: mass density, specific free energy, specific entropy, strain and Cauchy's stress,
- $\epsilon, \epsilon_\alpha^{pf}$ overall strain and intrinsic inelastic strain in the phase α ,
- $\dot{\epsilon}_\alpha^p, \dot{\epsilon}_\alpha^{ip}$ intrinsic plastic strain rate and transformation plasticity strain rate of the phase α ,
- $\epsilon_*^{pf}, \dot{\epsilon}_*^{pf}, \dot{\epsilon}_{ip}$ overall: permanent strain, inelastic strain rate and transformation plasticity strain rate,
- $\dot{q}, \dot{D}, \dot{W}, \dot{W}^{(0)}$ rate of: heat supply, energy dissipation, actual and reversible work,
- b_K^α, h_α metallography and inelastic internal parameters,

F^α yield function of the phase α ,
 $\Lambda_k, \Lambda^\alpha$ Lagrange's multipliers.

Notation

$\mathbf{A} \cdot \mathbf{B} \rightarrow A_{ij} B_{ij}$,
 $\mathbf{AB} \rightarrow A_{ijkl} B_{kl}$ or $A_{ij} B_j$,
 $\mathbf{A} \otimes \mathbf{B} \rightarrow A_i B_j$ (dyadic product),
 $\mathbf{1}$ fourth order unit tensor (symmetric),
 \mathbf{A}^{-1} inverse of \mathbf{A} ,
 \mathbf{A}^T transpose of \mathbf{A} .

1. Introduction

WHEN A SMALL PIECE of a metallic solid undergoes structural transformations it changes its physical properties, its shape and its volume. It is observed that volumetric changes are dominant if the external loads are not applied. However, the resulting deviatoric strains are of the same order when transformations proceed under applied stress, even if the stress is much smaller than the yield limit of the weakest phase. This distortional strain effect has been termed an overall „transformation-induced plasticity” (TRIP). It has been confirmed experimentally by many researchers (see e.g., [1, 6, 25]) and it is associated with nucleation and growth transformations (e.g., austenite \rightarrow pearlite in steels) and athermal transformations (e.g., austenite \rightarrow martensite). It is well known that volumetric and distortional strain effects accompanying phase transformations, together with ordinary thermal contraction (expansion) and plastic straining, are main and equally important sources of transient and residual stresses that occur in solid elements in the course of heat-treatment operations, welding, or chilling of castings. Therefore, during last 3 decades much attention has been devoted to modeling of the material behaviour under ongoing or finished phase transformations that are caused by variable thermo-mechanical loading (see e.g., [2, 12, 14, 15, 23, 29] and [30, 31]), and INOUE [26] has proposed to call this domain „metallo-thermo-mechanics”. The full set of constitutive equations of this domain consists of:

kinetic equations for representative metallography parameters, including weight (or volume) fractions of structural constituents (kinetics laws of phase transformations):

kinetic equations for hardening parameters;

rate equations for total strain (or stress) containing the usual term of thermo-elasto-plasticity and a term representing strain effects associated with phase transformations;

rate equation for temperature.

All equations are coupled since, e.g., stress influences the transformation kinetics, temperature depends on heat of phase formations and strain-rate depends on changes in the amount of phases ([20–21]). When plastic strains caused by mechanical means are large, this set of equations should also incorporate an effect known as „strain-induced phase transformations” (see e.g., [16, 17, 24]). The modeling is additionally impeded by the fact that the constitutive equations are supposed to be valid for a large temperature range (e.g. from austenitizing temperature down to room temperature).

In this paper we present the thermodynamical foundations for metallo-thermomechanics. An „ideal” metallic element is regarded as closed multiphase, multicomponent system being in constrained equilibrium at every instant during thermomechanical loading. Individual phases are treated as open elastic-ideal plastic subsystems (Sect. 3). Since we believe that differences between overall stresses and mean stresses acting over the colony of all individual phases are instrumental in explanation of TRIP, we suppose that the internal state of a macro-element can be described by the set of intrinsic elastic strains — each representing the mean elastic strain of some phase, and the set of dependent metallography parameters: weight fractions of all phases and parameters representing their instantaneous chemical compositions (which can vary during diffusive phase transformation). The reference model is characterized by a simple linear relation between the overall strain and intrinsic elastic phase strains (Sect. 3.2). The possible way of a generalization that does not include this simplification is also discussed. In Sect. 2 the specific free energy function of an ideal single phase elastic-perfectly plastic metallic element is derived under the assumption that specific heat at constant elastic strains is independent of elastic strain and temperature what is acceptable at a temperature range above the usual Debye temperature. The present work complements works of GIUSTI [19] and INOUE and WANG [21] where uniform stress assumptions were adopted and possible variations of the chemical composition of individual phases were neglected. Finally, in Subsect. 3.8, the effect of initial extra-stress due to phase formation on transformation induced total strain is discussed.

2. Thermostatistics of elastic-ideal-plastic single phase, homogeneous element

2.1. State equations

i) Single-phase multicomponent element of the total mass M^α and volume V^α we shall treat as homogeneous, chemically inert, open thermodynamical system ([3, 7] and [13]). Following the concepts of classical thermodynamics we shall single out the following variables of constrained equilibrium:

a) Extensive variables

Φ_α — the total free energy of the single-phase metallic element of mass M^α ,

M_K^α — masses of the individual components constituting the single phase ($K = 1, \dots, r$),

$$(2.1) \quad M^\alpha = \sum_{K=1}^r M_K^\alpha,$$

E_α^e — six variables representing the tensor of thermodynamic elastic strain,

$$(2.2) \quad E_\alpha^e = M^\alpha \epsilon_\alpha^e,$$

where ϵ_α^e is the elastic strain of the phase α defined beneath.

b) Intensive variables

μ_K^α — chemical potential of the component K ,

T — thermodynamic temperature, and

$$(2.3) \quad \bar{\tau}_\alpha = \frac{V^\alpha}{M^\alpha} \bar{\sigma}_\alpha = \frac{1}{\rho^\alpha} \bar{\sigma}_\alpha$$

Kirchhoff stress tensor. Here $\bar{\sigma}_\alpha$ is the usual Cauchy stress tensor and ρ^α is the density of single-phase solid.

The Greek index α indicates the property of a phase. Since in this section we deal with single phase solid, it simply replaces „the name” of a phase (it is not a free index). The elastic strain tensor ϵ_α^e is assumed to be infinitesimal and it is defined operationally in the same manner as in the classical theory of plasticity: suppose that at generic instant t of homogeneous process of constrained equilibrium (configuration $K(t)$ — Fig. 1) all forces acting on macroelement

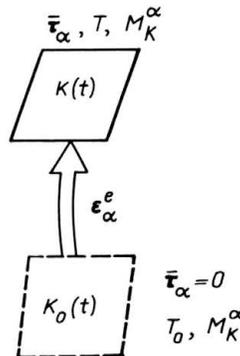


FIG. 1.

are released and its temperature is reduced to certain reference temperature T_0 , keeping the masses M_K^z of all components fixed. At the termination of this conceptual process an element will be in a new, so-called „natural state” of constrained equilibrium, and it will adopt the new configuration $K_0(t)$. The symmetric tensor variable that describe the shape of the element in configuration K with respect to its shape in K_0 is called the elastic strain tensor (Fig. 1).

ii) Here we neglect the free energy locked in the alloy element due to possible development of micro-stresses, defects creation etc., which (at small strains) is normally a small fraction of the total plastic work done on the element. This is one of the main simplifications that is employed when using so-called elastic-ideal plastic models. In other words, we assume that the difference of free energy at two different natural states is merely due to the formation of additional mass of a single phase solid (different M_K^z). Thus, the total free energy of a single phase solid is assumed to be the function of T , \mathbf{E}_α^e and M_K^z ($K = 1, \dots, r$) alone

$$(2.4) \quad \Phi_\alpha = \Phi_\alpha(T, \mathbf{E}_\alpha^e, M_K^z).$$

Accordingly we stipulate the Gibb's fundamental equation of state in the form

$$(2.5) \quad d\Phi_\alpha = -S_\alpha dT + \bar{\tau}_\alpha \cdot d\mathbf{E}_\alpha^e + \sum_{K=1}^r \mu_K^\alpha dM_K^\alpha,$$

where S_α is the total entropy of a metallic element. The corresponding thermal equations of state are

$$(2.6) \quad -S_\alpha = \frac{\partial \Phi_\alpha}{\partial T}, \quad \bar{\tau}_\alpha = \frac{\partial \Phi_\alpha}{\partial \mathbf{E}_\alpha^e}, \quad \mu_K^\alpha = \frac{\partial \Phi_\alpha}{\partial M_K^\alpha},$$

and μ_K^α represents the change in the total free energy when the mass M_K^α of component K is dissolved in phase α of the solid under constant \mathbf{E}_α^e and T .

Since Φ_α , \mathbf{E}_α^e , M_K^α are the extensive properties, the function Φ_α must be homogeneous function of order one with respect to \mathbf{E}_α^e and M_K^α . Hence

$$(2.7) \quad \Phi_\alpha = \bar{\tau}_\alpha \cdot \mathbf{E}_\alpha^e + \sum_{K=1}^r \mu_K^\alpha M_K^\alpha,$$

$$S_\alpha dT + \mathbf{E}_\alpha^e \cdot d\bar{\tau}_\alpha + \sum_{K=1}^r M_K^\alpha d\mu_K^\alpha = 0.$$

Equations (2.7)₁, and (2.7)₂ are called Euler relation and Gibbs–Duhem relation, respectively (see e.g., [3]), and the latter implies that there exists at least one scalar relationship between intensive quantities T , $\bar{\tau}_\alpha$ and μ_K^α what is the direct consequence of the homogeneity property of the function Φ_α .

iii) Introduce the *specific* free energy ϕ^α of single phase metallic element, $\phi^\alpha = \Phi_\alpha/M^\alpha$. Dividing (2.7) by M^α one obtains

$$(2.8) \quad \phi^\alpha = \bar{\tau}_\alpha \cdot \varepsilon_\alpha^e + \sum_{K=1}^r \mu_K^\alpha x_K^\alpha,$$

$$s^\alpha dT + \varepsilon_\alpha^e \cdot d\bar{\tau}_\alpha + \sum_{K=1}^r x_K^\alpha d\mu_K^\alpha = 0,$$

which are the Euler and Gibbs–Duhem relations written in the specific free energy representation, respectively. Likewise, calculating total differential $d\phi^\alpha$ (Eq. (2.8)₁) and using (2.8)₂ one arrives at the Gibb's fundamental equation expressed in terms of specific free energy

$$(2.9) \quad d\phi^\alpha = -s^\alpha dT + \bar{\tau}_\alpha \cdot d\varepsilon_\alpha^e + \sum_{K=1}^r \mu_K^\alpha dx_K^\alpha.$$

Here $s^\alpha = S^\alpha/M^\alpha$ and $x_K^\alpha = M_K^\alpha/M^\alpha$ are specific entropy and mass fraction of the component K ($K = 1, \dots, r$) in single phase alloy, respectively, so that

$$(2.10) \quad \sum_{K=1}^r x_K^\alpha = 1.$$

Suppose that the specific free energy ϕ^α has been experimentally determined as an arbitrary function (i.e., not necessary homogeneous) of variables T , ε_α^e and x_K^α . Then the total free energy Φ_α is also specified due to simple substitution

$$(2.11) \quad M^\alpha \phi^\alpha(T, \varepsilon_\alpha^e, x_K^\alpha) \Big|_{\varepsilon_\alpha^e = \mathbf{E}_\alpha^\alpha / M^\alpha} = \Phi_\alpha(T, \mathbf{E}_\alpha^\alpha, M_K^\alpha).$$

It is a homogeneous function of order one with respect to \mathbf{E}_α^α , M_K^α , on account (of 2.1). The inverse procedure is obvious because of the homogeneity property of the function Φ_α .

In what follows we shall be concerned with the specific free energy representation. Because x_K^α are not independent and they have to satisfy the constraint relation (2.10), we shall use the technique of Lagrange's multipliers to derive thermal equations of state. From Eq. (2.9) it follows that

$$(2.12) \quad s^\alpha = -\frac{\partial \phi^\alpha}{\partial T}(T, \varepsilon_\alpha^e, x_K^\alpha), \quad \bar{\tau}_\alpha = \frac{\partial \phi^\alpha}{\partial \varepsilon_\alpha^e}$$

and

$$(2.13) \quad f_K^\alpha \equiv \frac{\partial \phi^\alpha}{\partial x_K^\alpha} = \mu_K^\alpha - \mu^\alpha, \quad \mu^\alpha = \phi^\alpha - \bar{\tau}_\alpha \cdot \varepsilon_\alpha^e - \sum_{K=1}^r f_K^\alpha x_K^\alpha,$$

where the expression for the Lagrange's multiplier μ^α is calculated from (2.8)₁. Equation (2.13) enables to calculate the chemical potentials μ_K^α when intensive variables f_K^α are prescribed. This connection can also be found by direct calculation of partial derivatives of Eq. (2.11) with respect to M_K^α . Since $\sum_{K=1}^r \mu^\alpha dx_K^\alpha = 0$ the work of the thermodynamical force μ^α does not contribute to the free energy. The affinities associated with f_K^α and μ_K^α are, of course, the same since $\mu_K^\alpha - \mu_J^\alpha = f_K^\alpha - f_J^\alpha$ for $K \neq J$.

2.2. The free energy of single phase solid at temperature range above the Debye temperature

i) Above the Debye temperature the specific heat at constant volume for many metal components are practically constant. It is, therefore, plausible to stipulate that in this temperature range the specific heat c_ε^α at constant elastic strain of single phase solid will be the function of the composition x_K^α alone.

$$(2.14) \quad c_\varepsilon^\alpha = c_\varepsilon^\alpha(x_K^\alpha), \quad K = 1, \dots, r.$$

Since

$$(2.15) \quad c_\varepsilon^\alpha = T \frac{\partial s^\alpha}{\partial T}(T, \varepsilon_\alpha^e, x_K^\alpha) \quad \text{and} \quad \bar{\tau}_\alpha = 0 \quad \text{for} \quad T = T_0 \quad \text{and} \quad \varepsilon_\alpha^e = 0$$

according to the definitions of specific heat and the tensor of elastic strain, the free energy function must have the form

$$(2.16) \quad \phi^\alpha = c_\varepsilon^\alpha(x_K^\alpha)(T - T_0) - c_\varepsilon^\alpha(x_K^\alpha) T \ln \frac{T}{T_0} - (T - T_0) s_\varepsilon^\alpha(\varepsilon_\alpha^e, x_K^\alpha) + \phi_\varepsilon^\alpha(\varepsilon_\alpha^e, x_K^\alpha) - T \bar{s}^{\alpha*}(x_K^\alpha) + \bar{u}_\alpha^*(x_K^\alpha),$$

where

$$(2.17) \quad s_\varepsilon^\alpha = 0, \quad \phi_\varepsilon^\alpha = 0 \quad \text{and} \quad \frac{\partial \phi_\varepsilon^\alpha}{\partial \varepsilon_\alpha^e} = 0 \quad \text{for} \quad \varepsilon_\alpha^e = 0.$$

The specific entropy is of the form

$$(2.18) \quad s^\alpha = c_\varepsilon^\alpha(x_K^\alpha) \ln \frac{T}{T_0} + s_\varepsilon^\alpha(\varepsilon_\alpha^e, x_K^\alpha) + \bar{s}^{\alpha*}(x_K^\alpha).$$

Thus, the term s_ε^α represents the entropy change due to elastic straining of single-phase α at temperature T_0 , whereas $\bar{s}^{\alpha*}(x_K^\alpha)$ describes the entropy at $T = T_0 = 0$ and $\varepsilon_\alpha^e = 0$ (i.e., at natural state) which also includes so-called

entropy of mixing. The function $\phi_\varepsilon^\alpha(\varepsilon_\alpha^e, x_K^\alpha)$ describes the increase of the specific free energy due to elastic straining of a single phase alloy at $T = T_0$. It can thus be termed its *elastic potential energy* at $T = T_0$. The function $\bar{u}_\alpha^*(x_K^\alpha)$ and the term $\bar{u}_\alpha^*(x_K^\alpha) - T_0 \bar{s}^{\alpha*}(x_K^\alpha)$ represent the specific internal energy and specific free energy of a solid at natural state ($T = T_0, \bar{\varepsilon}_\alpha = 0, \varepsilon_\alpha^e = 0$), respectively.

Denote by β_α the tensor of elastic thermal stresses expressed in units of work per unit of mass per $^\circ K$ (energetic elastic thermal stresses), and by L_α the tensor of isothermal elastic stiffness expressed in terms of units of work per unit of mass (energetic elastic stiffness)

$$(2.19) \quad \beta_\alpha = -\frac{\partial \bar{\varepsilon}_\alpha}{\partial T} = \frac{\partial s_\varepsilon^\alpha}{\partial \varepsilon_\alpha^e}, \quad L_\alpha \equiv \frac{\partial \bar{\varepsilon}_\alpha}{\partial \varepsilon_\alpha^e}, \quad \bar{\varepsilon}_\alpha = \frac{\partial \phi_\varepsilon^\alpha}{\partial \varepsilon_\alpha^e} - (T - T_0) \frac{\partial s_\varepsilon^\alpha}{\partial \varepsilon_\alpha^e}.$$

It is seen that Eq. (2.14) implies that elastic stiffness tensor of a solid may be at *most linear function of the temperature*, whereas the *elastic thermal stresses are independent of the temperature* and are merely the functions of ε_α^e and the instantaneous chemical composition of single-phase metallic element.

The elastic behaviour of most of metallic solids may be approximated with rather good accuracy by linear relationship between $\bar{\varepsilon}_\alpha$ and ε_α^e at every T . Taking this for granted, the tensor L_α may be presented in the form

$$(2.20) \quad L_\alpha = L_\alpha^0(x_K^\alpha) - (T - T_0) \bar{L}_\alpha(x_K^\alpha).$$

Comparing Eqs. (2.19)₂ and (2.20) and using Eq. (2.19)₁ we get

$$(2.21) \quad \frac{\partial^2 s_\varepsilon^\alpha}{\partial \varepsilon_\alpha^{e2}} = \bar{L}_\alpha \rightarrow s_\varepsilon^\alpha = \frac{1}{2} \varepsilon_\alpha^e \cdot \bar{L}_\alpha \varepsilon_\alpha^e + \beta_\alpha^0(x_K^\alpha) \cdot \varepsilon_\alpha^e,$$

$$(2.22) \quad \frac{\partial^2 \phi_\varepsilon^\alpha}{\partial \varepsilon_\alpha^{e2}} = L_\alpha^0(x_K^\alpha) \rightarrow \phi_\varepsilon^\alpha = \frac{1}{2} \varepsilon_\alpha^e \cdot L_\alpha^0 \varepsilon_\alpha^e$$

on account of Eq. (2.17). Hence

$$(2.23) \quad \beta_\alpha = \beta_\alpha^0(x_K^\alpha) + \bar{L}_\alpha(x_K^\alpha) \varepsilon_\alpha^e,$$

where β_α^0 is the thermal stress at $\varepsilon_\alpha^e = 0$. Thus, we arrive at the conclusion that due to Eq. (2.20) and (2.14), the tensor of elastic thermal stresses may be at most linear function of ε_α^e .

The specific free energy function now takes the final form

$$(2.24) \quad \phi^\alpha = \frac{1}{2} \varepsilon_\alpha^e \cdot L_\alpha \varepsilon_\alpha^e - (T - T_0) \beta_\alpha^0(x_K^\alpha) \cdot \varepsilon_\alpha^e + c_\varepsilon^\alpha(x_K^\alpha)(T - T_0) - c_\varepsilon^\alpha(x_K^\alpha) T \ln \frac{T}{T_0} - T \bar{s}^{\alpha*}(x_K^\alpha) + \bar{u}_\alpha^*(x_K^\alpha).$$

On account of Eq. (2.24), the two basic thermal equations of state are

$$(2.25) \quad \begin{aligned} \bar{\tau}_\alpha &= \mathbf{L}_\alpha \boldsymbol{\varepsilon}_\alpha^e - (T - T_0) \boldsymbol{\beta}_\alpha^0(x_K^\alpha) = \mathbf{L}_\alpha^0 \boldsymbol{\varepsilon}_\alpha^e - (T - T_0) \boldsymbol{\beta}_\alpha(x_K^\alpha, \boldsymbol{\varepsilon}_\alpha^e), \\ s^\alpha &= c_\alpha^\alpha(x_K^\alpha) \ln \frac{T}{T_0} + \frac{1}{2} \boldsymbol{\varepsilon}_\alpha^e \cdot \bar{\mathbf{L}}_\alpha \boldsymbol{\varepsilon}_\alpha^e + \boldsymbol{\beta}_\alpha^0(x_K^\alpha) \cdot \boldsymbol{\varepsilon}_\alpha^e + s^{*\alpha}. \end{aligned}$$

The two assumptions, (2.14) and linearity of $\bar{\tau}_\alpha \rightarrow \boldsymbol{\varepsilon}_\alpha^e$ relation, are sufficient to specify the basic thermodynamical potential in terms of its natural variables with accuracy to two arbitrary functions of the chemical composition of single-phase solid element. However, the main importance of the above discussion for the engineering practice is as follows:

In the analysis of stresses occurring in single phase alloy during chilling process associated with large temperature drop (above the Debye temperature), one can assume definite temperature-dependence of all thermoelastic properties what considerably reduces the number of constants to be known when formulating the boundary-value problem. Since the thermal expansion tensor is more frequently used than $\boldsymbol{\beta}$, we shall now discuss the implications of the two main assumptions with reference to this quantity.

Denote by $\mathbf{M}_\alpha(T, x_K^\alpha)$ the tensor of isothermal elastic compliances of the single-phase solid

$$(2.26) \quad \mathbf{M}_\alpha \mathbf{L}_\alpha = \mathbf{1},$$

where $\mathbf{1}$ is the fourth-rank unit tensor, and write the inverse Hooke's law in the form,

$$(2.27) \quad \boldsymbol{\varepsilon}_\alpha^e = \mathbf{M}_\alpha \bar{\tau}_\alpha + (T - T_0) \bar{\boldsymbol{\alpha}}_\alpha(T, x_K^\alpha),$$

where

$$(2.28) \quad \bar{\boldsymbol{\alpha}}_\alpha \equiv \mathbf{M}_\alpha \boldsymbol{\beta}_\alpha^0(x_K^\alpha)$$

is so-called secant (engineering) thermal expansion tensor defined in the chosen natural state. It is seen that temperature-dependence of $\bar{\boldsymbol{\alpha}}_\alpha$ is the same as the temperature-dependence of inverse tensor to \mathbf{L}_α , which itself is linear function of T . In thermodynamics one employs the tangent thermal expansion tensor $\boldsymbol{\alpha}_\alpha$ defined by

$$(2.29) \quad \left. \frac{\partial \boldsymbol{\varepsilon}_\alpha^e}{\partial T} \right|_{\bar{\tau}_\alpha = \text{const}} \equiv \boldsymbol{\alpha}_\alpha = \mathbf{M}_\alpha \boldsymbol{\beta}_\alpha.$$

Combining Eqs. (2.23), (2.27) and (2.29) one can easily express $\boldsymbol{\alpha}_\alpha$ in terms of $\bar{\tau}_\alpha$, T and x_K^α ,

$$(2.30) \quad \begin{aligned} \alpha_\alpha &= \alpha_\alpha^0 + \mathbf{M}_\alpha \bar{\mathbf{L}}_\alpha \mathbf{M}_\alpha \bar{\tau}_\alpha, \\ \alpha_\alpha^0 &= [\mathbf{1} + (T - T_0) \mathbf{M}_\alpha \bar{\mathbf{L}}_\alpha] \bar{\alpha}_\alpha, \end{aligned}$$

where α_α^0 is the thermal expansion tensor at stress-free state. It is seen that the main two assumptions imply at most linear dependence of tangent thermal expansion tensor on the stresses. Equations (2.28) and (2.30) imply again the definite temperature-dependence of α_α^0 . Using (2.29) one can express β^α in terms of $\bar{\tau}_\alpha$, T and x_K^α ,

$$(2.31) \quad \beta_\alpha = \beta_\alpha^0 + \bar{\mathbf{L}}_\alpha \mathbf{M}_\alpha [\bar{\tau}_\alpha + (T - T_0) \beta_\alpha^0].$$

For further reference we shall also derive the internal energy $u^\alpha = \phi^\alpha + Ts^\alpha$,

$$(2.32) \quad \begin{aligned} u^\alpha &= \bar{u}_\alpha^*(x_K^\alpha) + u_1^\alpha(T, \epsilon_\alpha^e, x_K^\alpha), \\ u_1^\alpha &= c_\epsilon^\alpha(T - T_0) + T_0 \beta_\alpha^0 \cdot \epsilon_\alpha^e + \frac{1}{2} \epsilon_\alpha^e \cdot [\mathbf{L}_\alpha^0 + T_0 \bar{\mathbf{L}}_\alpha] \epsilon_\alpha^e. \end{aligned}$$

This function is obviously not a thermodynamical potential since the natural variables for u^α are s^α , ϵ_α^e and x_K^α . Note that $u^\alpha(T, \epsilon_\alpha^e, x_K^\alpha)$ is independent of entropy of mixing.

ii) We shall now briefly discuss the invariance property of the presented equations when the reference temperature T_0 is changed into

$$(2.33) \quad T'_0 = T_0 + \Delta T.$$

Denote by "prime" all quantities associated with new reference temperature T'_0 . Relations between elastic strains defined with reference to different temperatures are

$$(2.34) \quad \epsilon_\alpha^{e'} = \epsilon_\alpha^e - \Delta \epsilon_\alpha^e, \quad \Delta \epsilon_\alpha^e = \Delta T \mathbf{M}_\alpha(T'_0, x_K^\alpha) \beta_\alpha^0 = \Delta T \bar{\alpha}_\alpha(T'_0, x_K^\alpha).$$

All thermodynamic properties (i.e., those quantities that are derivatives of free energy function with respect to its natural variables) are, of course, invariant under transformation (2.33)

$$(2.35) \quad \mathbf{L}'_\alpha = \mathbf{L}_\alpha, \quad \mathbf{M}'_\alpha = \mathbf{M}_\alpha, \quad \bar{\mathbf{L}}'_\alpha = \bar{\mathbf{L}}_\alpha, \quad \beta'_\alpha = \beta_\alpha, \quad \alpha'_\alpha = \alpha_\alpha.$$

The transformations rules for other quantities are

$$(2.36) \quad \begin{aligned} \beta_\alpha^{0'} &= \mathbf{L}_\alpha^0 \mathbf{M}(T'_0, x_K^\alpha), \quad \mathbf{L}_\alpha^{0'} = \mathbf{L}_\alpha^0 - \Delta T \bar{\mathbf{L}}_\alpha, \\ \bar{s}^{\alpha'}(x_K^\alpha) &= \bar{s}^\alpha + c_\epsilon^\alpha \ln \left(\frac{T'_0}{T_0} \right) + s_\epsilon^\alpha (\Delta \epsilon_\alpha^e, x_K^\alpha), \quad \bar{u}_\alpha^{*'}(x_K^\alpha) = \bar{u}_\alpha^* + u_1^\alpha(T'_0, \Delta \epsilon_\alpha^e, x_K^\alpha), \\ \bar{\alpha}_\alpha &= \mathbf{M}_\alpha(T'_0, x_K^\alpha) \mathbf{L}_\alpha^0 \bar{\alpha}_\alpha. \end{aligned}$$

To prove the last relation note that Eq. (2.36)₁ is valid for arbitrary couple T_0 and T'_0 . It can also be shown that the difference between the thermal strains measured with respect to different reference temperature is constant,

$$(T - T_0)\bar{\alpha}_\alpha - (T - T'_0)\bar{\alpha}'_\alpha = \Delta\varepsilon_\alpha^e.$$

Moreover, the free energy, being itself invariant, preserves its mathematical form, i.e., unprimed quantities occurring in (2.24) can be replaced by the primed one.

If T_0 is the temperature at which the phase is formed then \bar{u}_α^* and \bar{s}_α^* can be presented in the form

$$(2.37) \quad \begin{aligned} \bar{u}_\alpha^* &= \sum_{K=1}^r x_K^\alpha u_{0\alpha}^K, \\ \bar{s}_\alpha^* &= \bar{s}_1^* + \bar{s}_0^*, \quad \bar{s}_1^* = \sum_{K=1}^r x_K^\alpha \bar{s}_K^*(x_J^\alpha), \quad \bar{s}_0^* = \sum_{K=1}^r x_K^\alpha s_{0K}^\alpha, \end{aligned}$$

where $\bar{s}_K^* = 0$ whenever $x_K^\alpha = 1$ ($x_J^\alpha = 0$ for $J \neq K$), and $x_K^\alpha \bar{s}_K^* \rightarrow 0$ when $x_K^\alpha \rightarrow 0$ ($K = 1, \dots, r$).

The term \bar{s}_1^* represents *entropy of mixing*, [13], i.e., the entropy associated with the formation of single phase alloy, which most commonly is the solid solution, and $u_{0\alpha}^K$ and s_{0K}^α are constants. The entropy of mixing has a well-supported basis in the statistical thermodynamics. For the phases that are "nonideal solutions" it is customary to stipulate the function \bar{s}_K^* in the form, [4],

$$(2.38) \quad \bar{s}_K^* = -R r_K^\alpha \ln \left[\frac{\gamma_K^\alpha r_K x_K^\alpha}{\sum_{J=1}^r r_J x_J^\alpha} \right],$$

where R is the universal gas constant, $r_K = 1/m_K$, m_K is the molar mass of the component K , and γ_K^α is the activity coefficient of the component K in the single phase α . The latter coefficient may be a function of composition x_K^α such that $\gamma_K^\alpha = 1$, whenever $x_K^\alpha = 1$. It can be deduced from the equilibrium diagram for the particular alloy.

3. Thermodynamics of elastic-plastic multicomponent multiphase metallic element

3.1. Constraint equations. Mean strain and mean stress

i) Consider a multiphase, multicomponent (r -components) metallic element (of total fixed mass M) that at generic instant t during thermo-mechanical process of deformation, associated with the internal diffusion of some components and phase changes, possesses n phases and occupies the volume $V(t)$ (Fig. 2). The element is assumed to be enclosed by a diathermal wall

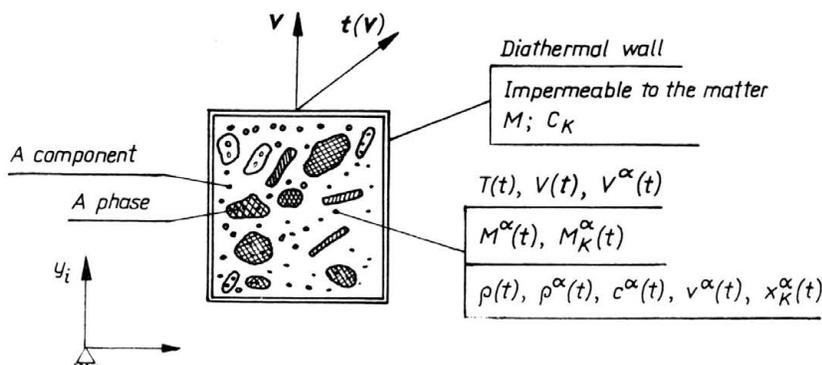


FIG. 2.

impermeable to the matter. Its instantaneous temperature is $T(t)$, whereas its chemical composition $C_K = M_K/M$ (M_K – total mass of the component K ; $K = 1, \dots, r$) is fixed. However, the individual phases are treated as open subsystems to the flow of the matter, and their chemical compositions $x_K^\alpha = M_K^\alpha(t)/M^\alpha(t)$ are varying in time. Here $M_K^\alpha(t)$ ($\alpha = 1, \dots, n$, $K = 1, \dots, r$) is the instantaneous mass of the component K in the phase α and $M^\alpha(t)$ the total mass of this phase $M^\alpha = \sum_{K=1}^r M_K^\alpha$. We employ the following notation: the Greek

indices indicate the property or quantity that refer to the phase. When the specific number of this index needs to be prescribed, it will be enclosed by brackets. Likewise, the indices denoted by Latin letters will indicate the property of the component. However, the concrete value of this index will not be placed into brackets. For example, the symbol $x_1^{(2)}$ denotes the weight fraction of the component no. 1 in the phase no. 2.

Introduce the symbols $\rho(t)$, $\rho^\alpha(t)$, $v^\alpha(t)$ and $c^\alpha(t)$ to denote mean mass density of the element, mean mass density of the phase α , volume, and mass fractions of the phase α , respectively, i.e., $\rho = M/V$, $\rho^\alpha = M^\alpha(t)/V(t)$, $v^\alpha = V^\alpha(t)/V(t)$ and $c^\alpha = M^\alpha/M$, where $V^\alpha(t)$ is the instantaneous total volume occupied by the phase α .

Note that

$$(3.1) \quad \sum_{\alpha=1}^n c^\alpha(t) x_K^\alpha(t) = C_K, \quad \sum_{K=1}^r x_K^\alpha(t) = 1,$$

$$\sum_{\alpha=1}^n (x_K^\alpha dc^\alpha + c^\alpha dx_K^\alpha) = 0, \quad \sum_{K=1}^r dx_K^\alpha = 0,$$

and since $\sum_{K=1}^r C_K = 1$, from Eq. (3.1)₁ it follows that $\sum_{\alpha=1}^n c^\alpha = 1$.

Hence in the set (x_k^α, c^α) containing $n(r+1)$ variables there are only $r(n-1)$ variables independent. Equations (3.1)₁ constitute the constraints for the variables that represent the chemical composition of individual phases and the weight fractions of the phases in the heterogeneous metallic element.

ii) Let $\hat{\rho}(y, t)$ be the local mass density distribution within the element, where y is the local position vector. From the definition of the mean mass density it follows that

$$(3.2) \quad \rho = \sum_{\alpha=1}^n \rho^\alpha v^\alpha, \quad \rho = \frac{1}{V(t)} \int \hat{\rho}(y, t) dV, \quad \rho^\alpha = \frac{1}{V^\alpha(t)} \int \hat{\rho} dV.$$

Likewise, the mean specific volume of macro-element and mean specific volumes of phase colonies are interrelated by

$$(3.3) \quad 1/\rho = \sum_{\alpha=1}^n c^\alpha/\rho^\alpha.$$

The connection between v^α , c^α and ratios of mean mass densities of all phases follows from

$$(3.4) \quad v^\alpha = \frac{\rho}{\rho^\alpha} c^\alpha$$

and Eq. (3.3) or (3.2)₁.

Introduce the matrix

$$(3.5) \quad l_{\alpha\beta} = 1 - \frac{\rho^\alpha}{\rho^\beta}, \quad \alpha, \beta = 1, \dots, n.$$

For some solids it is plausible to assume that all $l_{\alpha\beta}$ are *small quantities*. In this case, the ratio ρ^α/ρ can be evaluated from

$$(3.6) \quad \frac{\rho^\alpha}{\rho} = 1 + \sum_{\beta=1}^n l_{\beta\alpha} v^\beta + 0(|l_{\alpha\beta}|^2)$$

which is accurate to the first order in $l_{\beta\alpha}$. We note in passing that, to the same accuracy, $l_{\beta\alpha}$ is skew-symmetric ($l_{\alpha\beta} = -l_{\beta\alpha}$) and has at most $n-1$ independent elements since $l_{\alpha\beta} = l_{\alpha\gamma} - l_{\beta\gamma} + 0(|l_{\alpha\beta}|^2)$ for fixed γ . As a consequence

$$c^\alpha = \frac{\rho^\alpha}{\rho} v^\alpha \approx v^\alpha [1 + 0(|l_{\alpha\beta}|)]$$

i.e., in the first approximation c^α can be identified with v^α .

iii) Let $U(y, t)$ and $2E_{ij} = (\partial U_i/\partial y_j + \partial U_j/\partial y_i)$ denote the local fields of displacements and infinitesimal strains, respectively, and let \mathbf{T} be the instan-

taneous local field of Cauchy stresses that satisfy the equilibrium equations. The volume average strain (overall strain) is defined as

$$(3.7) \quad \boldsymbol{\varepsilon}(t) = \frac{1}{2V(t)} \int_A (\mathbf{U} \otimes \mathbf{v} + \mathbf{v} \otimes \mathbf{U}) dA = \frac{1}{V(t)} \int_V \mathbf{E} dV = \sum_{\alpha=1}^n v^\alpha \boldsymbol{\varepsilon}_\alpha,$$

where \mathbf{v} is the outward unit vector normal to the surface A of the macroelement (Fig. 2), and $\boldsymbol{\varepsilon}_\alpha$ are the volume mean strains in the phases $\alpha = 1, \dots, n$.

$$(3.8) \quad \boldsymbol{\varepsilon}_\alpha = \frac{1}{V^\alpha(t)} \int_{V^\alpha} \mathbf{E}(y, t) dV.$$

The mass average strain $\bar{\boldsymbol{\varepsilon}}(t)$ is

$$(3.9) \quad \bar{\boldsymbol{\varepsilon}}(t) = \frac{1}{M} \int_V \hat{\rho} \mathbf{E}(y, t) dV = \sum_{\alpha=1}^n c^\alpha \bar{\boldsymbol{\varepsilon}}_\alpha,$$

where

$$(3.10) \quad \bar{\boldsymbol{\varepsilon}}_\alpha = \frac{1}{M^\alpha(t)} \int_{V^\alpha} \hat{\rho}(y, t) \mathbf{E}(y, t) dV$$

is the mass mean strain in the phase α . Note that when the upper bounds $a_\alpha \geq |1 - \hat{\rho}/\rho^\alpha|$ estimating the deviation of the local mass density $\hat{\rho}(y, t)$ ($y \in V^\alpha$) from the mean values ρ^α ($\alpha = 1, \dots, n$) are small quantities, then

$$(3.11) \quad \bar{\boldsymbol{\varepsilon}}_\alpha = \boldsymbol{\varepsilon}_\alpha [1 + O(a_\alpha)] \approx \boldsymbol{\varepsilon}_\alpha,$$

and, if additionally $l_{\alpha\beta}$ are small, then also $\boldsymbol{\varepsilon} \approx \bar{\boldsymbol{\varepsilon}}$.

The overall Kirchhoff stress is defined as mass average of local Kirchhoff stress i.e.,

$$(3.12) \quad \boldsymbol{\tau} = \frac{1}{2M} \int_A (\mathbf{t} \otimes \mathbf{y} + \mathbf{y} \otimes \mathbf{t}) dA = \frac{1}{M} \int_{V(t)} \mathbf{T}(y, t) dV$$

so that

$$(3.13) \quad \boldsymbol{\tau} = \sum_{\alpha} c^\alpha \boldsymbol{\tau}_\alpha, \quad \boldsymbol{\tau}_\alpha = \frac{1}{M^\alpha(t)} \int_{V^\alpha} \mathbf{T}(y, t) dV,$$

where $\mathbf{t} = \mathbf{T}\mathbf{v}$ is the vector of surface tractions and $\boldsymbol{\tau}_\alpha$ is mass mean Kirchhoff stress in the phase α . It can easily be shown that volume averages of Cauchy stresses $\boldsymbol{\sigma}$ and $\boldsymbol{\sigma}_\alpha$ are related to $\boldsymbol{\tau}$ and $\boldsymbol{\tau}_\alpha$ by

$$(3.14) \quad \rho \boldsymbol{\tau} = \boldsymbol{\sigma}, \quad \rho^\alpha \boldsymbol{\tau}_\alpha = \boldsymbol{\sigma}_\alpha \quad (\boldsymbol{\sigma} = \sum_{\alpha=1}^n v^\alpha \boldsymbol{\sigma}_\alpha).$$

The overall specific free energy and specific entropy are defined as mass averages of the corresponding local fields $\hat{\phi}(y, t)$ and $\hat{s}(y, t)$

$$(3.15) \quad \begin{aligned} \phi &= \frac{1}{M} \int_V \hat{\rho}(y, t) \hat{\phi}(y, t) dV = \sum_{\alpha} c^{\alpha} \phi^{\alpha}, \\ s &= \frac{1}{M} \int_V \hat{\rho}(y, t) \hat{s}(y, t) dV = \sum_{\alpha} c^{\alpha} s^{\alpha}, \end{aligned}$$

where

$$\phi^{\alpha} = \frac{1}{M^{\alpha}} \int_{V^{\alpha}} \hat{\rho} \phi dV, \quad s^{\alpha} = \frac{1}{M^{\alpha}} \int_{V^{\alpha}} \hat{\rho} s dV$$

are mean specific free energy and entropy of the phase α , respectively.

3.2. Assemblage relations. Kinematical reference model

i) Restrict attention to a slow uniform straining process during which at the outer surface of an alloy element the displacement \mathbf{U} is prescribed in the form $\mathbf{U} = \boldsymbol{\varepsilon}^0(t) \mathbf{y}$, where $\boldsymbol{\varepsilon}^0 = \overset{T_0}{\boldsymbol{\varepsilon}^0}$ is independent of the surface particle, and heat exchange is sufficiently slow such that the local temperature distribution is close to its average value at every moment. According to Eq. (3.7)₁, the prescribed function $\boldsymbol{\varepsilon}^0(t)$ is equal to the mean strain in the element $\boldsymbol{\varepsilon}(t) = \boldsymbol{\varepsilon}^0(t)$. The local field equations should include the diffusion process of some components, formation of new phases, including the martensitic-type phases, plasticity, elasticity, as well as they should take into account the discontinuities of the thermo-mechanical properties at the movable phase boundaries. The solution to such high-complexity problem has not been found, so far. Therefore, at this stage of development of the theory, it is necessary to adopt certain model assumptions. These concern the relations that can possibly exist between mean strains $\boldsymbol{\varepsilon}_{\alpha}$ in the individual phases, mean total strain $\boldsymbol{\varepsilon}$ and temperature difference $T - T_0$ where T_0 is the initial temperature. We suppose that a set of small numbers $\eta_{\alpha\beta}$ can be distinguished that are all of the order of the differences between the mean thermal expansion coefficients of individual phases, so that the temperature dependence of $\boldsymbol{\varepsilon}_{\alpha}$ can be expressed in terms of $\eta_{\alpha\beta}(T - T_0)$ which are also small quantities. Then, since $\boldsymbol{\varepsilon}$ is small, one can expand such unknown relation into the Taylor series with respect to $\boldsymbol{\varepsilon}$ and $\eta_{\alpha\beta}(T - T_0)$.

$$(3.16) \quad \boldsymbol{\varepsilon}_{\alpha} = \mathbf{A}_{\alpha} \boldsymbol{\varepsilon} + \mathbf{B}_{\alpha} (T - T_0) + \boldsymbol{\varepsilon}_{\alpha}^{r1} + \mathbf{O}_{\alpha} (|\boldsymbol{\varepsilon}|^2, |\eta_{\alpha\beta}|^2),$$

where \mathbf{A}_{α} , \mathbf{B}_{α} and residual strain $\boldsymbol{\varepsilon}_{\alpha}^{r1}$ are all independent of $\boldsymbol{\varepsilon}$ and temperature. Neglecting the last term occurring in (3.16), they will be referred to as "assem-

blage relations". The assemblage tensors \mathbf{A}_α , \mathbf{B}_α and $\boldsymbol{\varepsilon}_\alpha^{r1}$ may depend on metallography parameters; we denote by b_k^α , such as x_k^α , c_α , mean grain size of the colony of phases α (in terms of which one can express the mean grain size of all phases), and parameters representing the shape and distributions of grains (e.g., continuity parameters, mean free distances between the discontinuous phases etc.) as discussed by TOMOTA and TAMURA [18]. The tensor $\boldsymbol{\varepsilon}_\alpha^{r1}$ may also depend on microshears in all active slip systems of all phases, and on all phase microstrains that can occur at all phase boundaries. The micro-shears and phase microstrains will probably have negligible influence on \mathbf{A}_α and \mathbf{B}_α since these two tensors modify significantly only overall thermoelastic properties of an element.

Since Eq. (3.16) must be consistent with Eq. (3.7)₃, the tensors \mathbf{A}_α , \mathbf{B}_α and $\boldsymbol{\varepsilon}_\alpha^{r1}$ should satisfy the conditions:

$$(3.17) \quad \sum_{\alpha=1}^n v^\alpha \mathbf{A}_\alpha = \mathbf{1}, \quad \sum_{\alpha=1}^n v^\alpha \mathbf{B}_\alpha = \mathbf{0}, \quad \sum_{\alpha=1}^n v^\alpha \boldsymbol{\varepsilon}_\alpha^{r1} = \mathbf{0},$$

where volume fractions v^α are functions of mass fractions of all phases given by Eq. (3.4). In particular

$$(3.18) \quad \begin{aligned} \mathbf{A}_\alpha &= \mathbf{1}, & \mathbf{B}_\alpha &= \mathbf{0}, & \boldsymbol{\varepsilon}_\alpha^{r1} &= \mathbf{0} & \text{when } c^\alpha &= 1, \\ v^\alpha \mathbf{A}_\alpha &\rightarrow \mathbf{0}, & v^\alpha \mathbf{B}_\alpha &\rightarrow \mathbf{0}, & v^\alpha \boldsymbol{\varepsilon}_\alpha^{r1} &\rightarrow \mathbf{0} & \text{when } c^\alpha &\rightarrow 0. \end{aligned}$$

ii) The partial elastic strain $\boldsymbol{\varepsilon}_\alpha^e$ in the phase α can be imagined as a mean elastic strain that could be measured after a thought process of cutting of all particles of the phase colony α out from a multiphase element and reducing their temperature to T_0 . We shall define the second residual strain $\boldsymbol{\varepsilon}_\alpha^{r2}$ by

$$(3.19) \quad \boldsymbol{\varepsilon}_\alpha^e = \boldsymbol{\varepsilon}_\alpha - \boldsymbol{\varepsilon}_\alpha^{r2}.$$

The tensor $\boldsymbol{\varepsilon}_\alpha^{r2}$ represents plastic microshears in the slip systems of the colony of the phase α alone, and it also includes the permanent microstrains that can occur at the boundaries of α -phase colony when small amount of the parent phase is transformed into the α -phase.

Combining Eqs. (3.16) and (3.19), the assemblage relations can be expressed in terms of $\boldsymbol{\varepsilon}_\alpha^e$

$$(3.20) \quad \boldsymbol{\varepsilon}_\alpha^e = \mathbf{A}_\alpha \boldsymbol{\varepsilon} + \mathbf{B}_\alpha (T - T_0) - \boldsymbol{\varepsilon}_\alpha^{pf},$$

where $\boldsymbol{\varepsilon}_\alpha^{pf} = \boldsymbol{\varepsilon}_\alpha^{r2} - \boldsymbol{\varepsilon}_\alpha^{r1}$ is the measure of the intrinsic inelastic strain in the phase α due to the thermo-mechanical interactions with other phases and due to phase transformations.

Note that ϵ_{α}^{pf} doesn't need to satisfy the conditions (3.17)₃.

iii) It is believed that the assemblage tensors A_{α} and B_{α} could be determined in the course of systematic experimental program. One can distinguish the "kinematical reference model" for which

$$(3.21) \quad A_{\alpha} = 1, \quad B_{\alpha} = 0, \quad \epsilon_{\alpha}^e = \epsilon - \epsilon_{\alpha}^{pf}$$

holds, and all constitutive functions are determined on the basis of available experimental data concerning the properties of individual phases. The possible difference between predictions of the kinematical reference model and experimental results obtained for multiphase alloy could subsequently be used to construct the higher priority model for which assumption (3.21) does not hold. Note that Eqs. (3.21) does not imply $\epsilon = \epsilon_{\alpha}$.

In what follows we shall be concerned only with the kinematical reference model. The possible generalization of this model that can also include other specified metallography parameters, e.g., mean grain size of the colony of the phase α , may be performed along the same line of reasoning, provided that the evolution law for such parameters are experimentally established.

3.3. Free energy and thermoelasticity tensors

i) According to Eq. (3.15)₁ and the assumption (3.21), the overall specific free energy of a multiphase element can be regarded as a function of T , ϵ , metallography internal parameters $b_K^{\alpha} = \{x_K^{\alpha}, c^{\alpha}\}$, and inelasticity internal parameters, which we denote by $h_{\alpha} = \{\epsilon_{\alpha}^{pf}\}$ ($\alpha = 1, \dots, n$, $K = 1, \dots, r$)

$$(3.22) \quad \phi(T, \epsilon, b_K^{\alpha}, h_{\alpha}) = \sum_{\beta=1}^n c^{\beta} \phi^{\beta}(T, \epsilon_{\beta}^e, x_K^{\beta}),$$

where ϕ^{β} has already been specified by Eq. (2.24), and ϵ_{α}^e is the simple function of ϵ and ϵ_{α}^{pf} given by Eq. (3.21)₃. More generally, one could add to ϕ so called configurational free energy that depends on c^{α} . Here, however this energy will be neglected. We shall now use the general thermodynamic framework developed by RICE [8], HILL and RICE [9], and RICE [10] with slight modifications following from the fact that b_K^{α} are dependent variables that have to satisfy constraint relations (3.1). It is convenient to use the technique of Lagrange's multipliers and to employ the function $\check{\phi}$ defined by

$$(3.23) \quad \check{\phi} = \phi + \sum_{\alpha}^n \left[\Lambda^{\alpha} \sum_K^r (x_K^{\alpha} - 1) \right] + \sum_K^r \left[\Lambda_K \left(\sum_{\alpha}^n c^{\alpha} x_K^{\alpha} - C_K \right) \right]$$

which assumes the same values as ϕ since the last two terms vanish, on account of Eq. (3.1). Here Λ^{α} and Λ_K are appropriate Lagrange multipliers. All variables will now be mathematically treated as independent.

Bearing in mind (3.13)₁ and (3.15)₂ we adopt the following Gibbs fundamental equation of state

$$(3.24) \quad d\check{\phi} = -s dT + dW^{(0)},$$

$$dW^{(0)} = \boldsymbol{\tau} \cdot d\boldsymbol{\varepsilon} - \sum_{\alpha=1}^n c^\alpha \boldsymbol{\tau}_\alpha \cdot d\boldsymbol{\varepsilon}_\alpha^{\text{pf}} + \sum_{\alpha=1}^n \check{f}^\alpha dc^\alpha + \sum_{\alpha,K}^{n,r} \check{f}_K^\alpha dx_K^\alpha,$$

where, $dW^{(0)}$ represents the increment of work in the conceptual reversible process, at each stage of which an element is in a state of constrained equilibrium, s is the specific entropy of an element, and $\boldsymbol{\tau}$ is an overall (average) Kirchhoff stress tensor. Note again that $d\phi = d\check{\phi}$, whenever state variable x_K^α and c^α satisfy the constraint relations (3.1)₁.

The thermal equations of state following from (3.24) are

$$(3.25) \quad s = -\frac{\partial\phi}{\partial T} = \sum_{\alpha=1}^n c^\alpha s^\alpha, \quad -s^\alpha = \frac{\partial\phi^\alpha}{\partial T},$$

$$\boldsymbol{\tau} = \frac{\partial\phi}{\partial\boldsymbol{\varepsilon}} = \sum_{\alpha=1}^n c^\alpha \boldsymbol{\tau}_\alpha, \quad \boldsymbol{\tau}_\alpha = \frac{\partial\phi^\alpha}{\partial\boldsymbol{\varepsilon}} = \frac{\partial\phi^\alpha}{\partial\boldsymbol{\varepsilon}_\alpha^e} = -\frac{\partial\phi^\alpha}{\partial\boldsymbol{\varepsilon}_\alpha^{\text{pf}}},$$

$$\check{f}^\alpha = \frac{\partial\check{\phi}}{\partial c^\alpha} = \phi^\alpha + \sum_{K=1}^r \Lambda_K x_K^\alpha,$$

$$\check{f}_K^\alpha = \frac{\partial\check{\phi}}{\partial x_K^\alpha} = c^\alpha f_K^\alpha + \Lambda^\alpha + \Lambda_K c^\alpha, \quad f_K^\alpha \equiv \frac{\partial\phi^\alpha}{\partial x_K^\alpha}.$$

Here $\boldsymbol{\tau}_\alpha$ is an intrinsic Kirchhoff stress in the phase α . Likewise, s^α is an intrinsic specific entropy of the phase α . For the considered kinematical reference model $\boldsymbol{\tau}_\alpha$ and s^α have the special form (2.25), where $\boldsymbol{\varepsilon}_\alpha^e = \boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_\alpha^{\text{pf}}$, and

$$(3.26) \quad \bar{\boldsymbol{\tau}}_\alpha = \boldsymbol{\tau}_\alpha.$$

ii) Since ϕ^α is independent of c^α , the kinematical reference model predicts the Voigt estimates for overall thermo-elastic properties of the multiphase metallic element:

the overall specific heat c_ε (cf. Eqs. (2.14), (2.15))

$$(3.27) \quad c_\varepsilon \equiv T \frac{\partial s}{\partial T} = \sum_{\alpha=1}^n c^\alpha c_\varepsilon^\alpha(x_K^\alpha),$$

the tensor of overall (energetic) isothermal elastic stiffness (cf. Eqs. (2.19), (2.20))

$$(3.28) \quad \mathbf{L} = \frac{\partial\boldsymbol{\tau}}{\partial\boldsymbol{\varepsilon}} = \sum_{\alpha=1}^n c^\alpha \mathbf{L}_\alpha = \mathbf{L}^0(c^\alpha, x_K^\alpha) - \bar{\mathbf{L}}(c^\alpha, x_K^\alpha)(T - T_0),$$

$$\mathbf{L}^0 = \sum_{\alpha=1}^n c^\alpha \mathbf{L}_\alpha^0(x_K^\alpha), \quad \bar{\mathbf{L}} = \sum_{\alpha=1}^n c^\alpha \bar{\mathbf{L}}_\alpha(x_K^\alpha),$$

$$(3.24) \quad d\check{\phi} = -sdT + dW^{(0)},$$

$$dW^{(0)} = \tau \cdot d\boldsymbol{\varepsilon} - \sum_{\alpha=1}^n c^\alpha \tau_\alpha \cdot d\boldsymbol{\varepsilon}_\alpha^{\text{pf}} + \sum_{\alpha=1}^n \check{f}^\alpha dc^\alpha + \sum_{\alpha,K}^{n,r} \check{f}_K^\alpha dx_K^\alpha,$$

where, $dW^{(0)}$ represents the increment of work in the conceptual reversible process, at each stage of which an element is in a state of constrained equilibrium, s is the specific entropy of an element, and τ is an overall (average) Kirchhoff stress tensor. Note again that $d\phi = d\check{\phi}$, whenever state variable x_K^α and c^α satisfy the constraint relations (3.1)₁.

The thermal equations of state following from (3.24) are

$$(3.25) \quad s = -\frac{\partial\phi}{\partial T} = \sum_{\alpha=1}^n c^\alpha s^\alpha, \quad -s^\alpha = \frac{\partial\phi^\alpha}{\partial T},$$

$$\tau = \frac{\partial\phi}{\partial\boldsymbol{\varepsilon}} = \sum_{\alpha=1}^n c^\alpha \tau_\alpha, \quad \tau_\alpha = \frac{\partial\phi^\alpha}{\partial\boldsymbol{\varepsilon}} = \frac{\partial\phi^\alpha}{\partial\boldsymbol{\varepsilon}_\alpha^e} = -\frac{\partial\phi^\alpha}{\partial\boldsymbol{\varepsilon}_\alpha^{\text{pf}}},$$

$$\check{f}^\alpha = \frac{\partial\check{\phi}}{\partial c^\alpha} = \phi^\alpha + \sum_{K=1}^r \Lambda_K x_K^\alpha,$$

$$\check{f}_K^\alpha = \frac{\partial\check{\phi}}{\partial x_K^\alpha} = c^\alpha f_K^\alpha + \Lambda^\alpha + \Lambda_K c^\alpha, \quad f_K^\alpha \equiv \frac{\partial\phi^\alpha}{\partial x_K^\alpha}.$$

Here τ_α is an intrinsic Kirchhoff stress in the phase α . Likewise, s^α is an intrinsic specific entropy of the phase α . For the considered kinematical reference model τ_α and s^α have the special form (2.25), where $\boldsymbol{\varepsilon}_\alpha^e = \boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_\alpha^{\text{pf}}$, and

$$(3.26) \quad \bar{\tau}_\alpha = \tau_\alpha.$$

ii) Since ϕ^α is independent of c^α , the kinematical reference model predicts the Voigt estimates for overall thermo-elastic properties of the multiphase metallic element:

the overall specific heat c_ε (cf. Eqs. (2.14), (2.15))

$$(3.27) \quad c_\varepsilon \equiv T \frac{\partial s}{\partial T} = \sum_{\alpha=1}^n c^\alpha c_\varepsilon^\alpha(x_K^\alpha),$$

the tensor of overall (energetic) isothermal elastic stiffness (cf. Eqs. (2.19), (2.20))

$$(3.28) \quad \mathbf{L} = \frac{\partial\tau}{\partial\boldsymbol{\varepsilon}} = \sum_{\alpha=1}^n c^\alpha \mathbf{L}_\alpha = \mathbf{L}^0(c^\alpha, x_K^\alpha) - \bar{\mathbf{L}}(c^\alpha, x_K^\alpha)(T - T_0),$$

$$\mathbf{L}^0 = \sum_{\alpha=1}^n c^\alpha \mathbf{L}_\alpha^0(x_K^\alpha), \quad \bar{\mathbf{L}} = \sum_{\alpha=1}^n c^\alpha \bar{\mathbf{L}}_\alpha(x_K^\alpha),$$

3.4. Rate form of the thermal equations of state

The rate form of the two basic thermal equations of internal state of individual phases can be obtained by calculating the time derivative of Eq. (2.25), or directly by using the definitions of L_α , c_α^e and β ,

$$(3.33) \quad \begin{array}{ccc} 1-1 & 2-1 & 3-1 \\ \downarrow & \downarrow & \downarrow \\ \dot{\tau}_\alpha = L_\alpha \dot{\epsilon} & - \beta_\alpha \dot{T} & - L_\alpha \dot{\epsilon}_\alpha^{pf} + \sum_{K=1}^r \tau_K^\alpha \dot{x}_K^\alpha, \end{array}$$

$$T \dot{s}^\alpha = T \beta_\alpha \cdot (\dot{\epsilon} - \dot{\epsilon}_\alpha^{pf}) + c_\alpha^e \dot{T} + T \sum_{K=1}^r s_K^\alpha \dot{x}_K^\alpha,$$

$$\begin{array}{ccc} \uparrow & \uparrow & \uparrow \\ 1-2 & 2-2 & 3-2 \end{array}$$

where

$$\tau_K^\alpha \equiv \frac{\partial \tau^\alpha}{\partial x_K^\alpha} = \frac{\partial f_K^\alpha}{\partial \mathbf{e}_\alpha^e}, \quad s_K^\alpha \equiv \frac{\partial s^\alpha}{\partial x_K^\alpha} = - \frac{\partial f_K^\alpha}{\partial T}$$

The individual terms represent the following intrinsic effects:

1-1 → intrinsic elasticity,

2-1 → elastic intrinsic thermal stresses,

3-1 → inelastic intrinsic stresses due to combined plastic and internal matter flows,

1-2 → heat of elastic strain,

2-2 → heat capacity,

3-2 → reversible intrinsic heat of single phase formation.

The corresponding rate equation for multiphase solid may be written in the similar form

$$(3.34) \quad \dot{\mathbf{t}} = \sum_{\alpha=1}^n (c^\alpha \tau_\alpha + c^\alpha \dot{\mathbf{t}}_\alpha) = \mathbf{L} \dot{\epsilon} - \beta \dot{T} - \dot{\mathbf{t}}^{pf}.$$

The first two terms represent the usual overall thermo-elastic stress increment, whereas the last term — the overall stress increment due to the plastic flow and all solid-solid phase transformations that take place within the element,

$$(3.35) \quad \dot{\mathbf{t}}^{pf} = \sum_{\alpha=1}^n (c^\alpha L_\alpha \dot{\epsilon}_\alpha^{pf} - c^\alpha \tau_\alpha) - \sum_{\alpha,K}^{n,r} c^\alpha \tau_K^\alpha \dot{x}_K^\alpha.$$

Likewise,

$$(3.36) \quad T \dot{s} = c_e \dot{T} + T \sum_{\alpha=1}^n c^\alpha \beta_\alpha \cdot (\dot{\boldsymbol{\varepsilon}} - \dot{\boldsymbol{\varepsilon}}_\alpha^{\text{pf}}) + T \sum_{\alpha=1}^n [s^\alpha \dot{c}^\alpha + c^\alpha \sum_{K=1}^r s_K^\alpha \dot{x}_K^\alpha].$$

The interpretation of individual terms is analogous to Eq. (3.33).

One can also introduce the notion of overall inelastic strain rate $\dot{\boldsymbol{\varepsilon}}^{\text{pf}}$ in analogous way as it is done in thermo-plasticity, [8, 22], (cf. Eq. (3.22))

$$(3.37) \quad \begin{aligned} \dot{\boldsymbol{\varepsilon}}^{\text{pf}} &\equiv \mathbf{M} \dot{\boldsymbol{\tau}}^{\text{pf}} = \sum_{\alpha, K}^{n, r} \frac{\partial \boldsymbol{\varepsilon}(T, \boldsymbol{\tau}, h_K^\alpha, h_\alpha)}{\partial h_K^\alpha} \dot{h}_K^\alpha + \sum_{\alpha=1}^n \frac{\partial \boldsymbol{\varepsilon}}{\partial h_\alpha} \dot{h}_\alpha \\ &= \sum_{\alpha=1}^n c^\alpha \mathbf{M} (\mathbf{L}_\alpha \dot{\boldsymbol{\varepsilon}}_\alpha^{\text{pf}}) - \sum_{\alpha=1}^n [c^\alpha \mathbf{M} \boldsymbol{\tau}_\alpha + c^\alpha \sum_{K=1}^r \mathbf{M} \boldsymbol{\tau}_K^\alpha \dot{x}_K^\alpha] \end{aligned}$$

so that

$$(3.38) \quad \dot{\boldsymbol{\varepsilon}} = \mathbf{M} \dot{\boldsymbol{\tau}} + \boldsymbol{\alpha} \dot{T} + \dot{\boldsymbol{\varepsilon}}^{\text{pf}}.$$

Here $\mathbf{M} = \mathbf{L}^{-1}$ is the overall (energetic) isothermal elastic compliance tensor, and $\boldsymbol{\alpha} = \mathbf{M} \boldsymbol{\beta}$ is the overall tangent thermal expansion tensor.

Again $\dot{\boldsymbol{\varepsilon}}^{\text{pf}}$ results from both plastic flow and phase transformations. The last term occurring in Eq. (3.37) is of the order of elastic strains. It constitutes a part of overall “transformation plasticity strain rate”. Note, that $\dot{\boldsymbol{\varepsilon}}^{\text{pf}} \neq \dot{\boldsymbol{\varepsilon}}_\star^{\text{pf}}$.

3.5. Unconstrained equilibrium with respect to the internal flow of matter

We shall now examine the properties of the discussed kinematical reference model at the unconstrained equilibrium with respect to the internal flow of matter at $T = \text{const}$ and $\boldsymbol{\varepsilon}_\alpha^e = \text{const}$ ($\alpha = 1, \dots, n$).

At equilibrium \check{f}^α and \check{f}_K^α must all vanish

$$(3.39) \quad \check{f}^\alpha = 0, \quad \check{f}_K^\alpha = 0.$$

Using the above set of $n(r+1)$ Eqs. (3.25)_{3,4} and (3.1), it is not difficult to express the equilibrium values of Lagrange’s multipliers Λ_K and Λ^α in terms of equilibrium compositions x_K^α of all phases and equilibrium amounts c^α of the phases

$$(3.40) \quad \Lambda^\alpha = c^\alpha [\phi^\alpha - \sum_{K=1}^r f_K^\alpha x_K^\alpha],$$

$$(3.41) \quad -\Lambda_K = f_K^\alpha + \phi^\alpha - \sum_{J=1}^r f_J^\alpha x_J^\alpha = \mu_K^\alpha + \boldsymbol{\tau}_\alpha \cdot \boldsymbol{\varepsilon}_\alpha^e,$$

where $\varepsilon_\alpha^e = \varepsilon - \varepsilon_\alpha^{pf}$ and μ_K^α is the usual chemical potential defined by Eq. (2.13). The set of $n(r+1)$ Eqs. (3.40) – (3.41) is, of course, equivalent to Eq. (3.39). The mathematical aspect that we shall discuss here is the following: suppose that $\varepsilon - \varepsilon_\alpha^{pf}$ and T are fixed. We check if the set of algebraic equations consisting of $n(r+1) + n+r$ Eqs. (3.40) – (3.41) and (3.1)₁ enables to find equilibrium values of $n(r+1) + n+r$ unknown Λ^α , Λ_K , x_K^α and c^α . We do not employ special symbols for equilibrium values, believing that this will not confuse the issue.

Let us note that the for the considered kinematical reference model Λ_K is independent of c^α since ϕ^α has this property, and that the set of $n \cdot r$ Eqs. (3.41) may be replaced by the following equivalent set of $n \cdot r$ equations

$$(3.42) \quad -\Lambda_K \cdot n = \sum_{\alpha=1}^n (\mu_K^\alpha + \tau_\alpha \cdot \varepsilon_\alpha^e),$$

$$(3.43) \quad \mu_K^{(1)} + \tau_{(1)} \cdot \varepsilon_{(1)}^e = \mu_K^{(2)} + \tau_{(2)} \cdot \varepsilon_{(2)}^e = \dots = \mu_K^{(n)} + \tau_{(n)} \cdot \varepsilon_{(n)}^e.$$

The Eqs. (3.43) constitute generalization of the well known equilibrium conditions ([7, 13]). At unconstrained equilibrium the generalized chemical potential $\bar{\mu}_K^\alpha = \mu_K^\alpha + \tau_\alpha \cdot \varepsilon_\alpha^e$ of every component must be the same in each phase.

Note (cf. Eq. (2.5)) that $\bar{\mu}_K^\alpha$ represents the change in the total free energy when the mass M_K^α of component K is dissolved in the phase α under constant ε_α^e and T .

To find equilibrium composition x_K^α and equilibrium amounts of phases c^α one can now use the set of $n \cdot r + n$ Eqs. (3.43) and (3.1), since Λ_K and Λ^α can subsequently be calculated from Eqs. (3.42) and (3.40), i.e. the initial set of equations have been solved with respect to Λ_K and Λ^α .

Because of the fact that the subset of $(n-1)r$ Eqs. (3.43) is independent of c^α , we have now to consider separately two cases:

i) $\nu \equiv n - r \leq 0$. When the number of phases is not greater than the number of components, the unconstrained equilibrium chemical compositions of all phases x_K^α and the equilibrium weight fractions c^α of the phases, may unambiguously be determined from the set of Eqs. (3.43) and (3.1). Thus, the so-called “lever rule” applied frequently in metallurgy may be meaningful only in this case.

ii) $\nu \equiv n - r > 0$. In this case, the subset of $(n-1)r + n$ Eqs. (3.1)₂ and (3.43), containing only the variables x_K^α (c^α are not present there), has more equations than unknown variables. Consequently, the physically meaningful equilibrium compositions x_K^α of the phases can be found only when ν -functional relationships between Eqs. (3.43) exist. In effect, equilibrium compositions of the phases can be determined if there exist ν relationship between T and τ_α (or $\varepsilon - \varepsilon_\alpha^{pf}$)

$$(3.44) \quad \Psi^{(L)}(T, \tau_\alpha) = 0, \quad L = 1, \dots, v.$$

Supposing that the intensive state variables satisfy Eqs. (3.44), the equilibrium compositions x_K^α can be found, and one can try to determine the amount of phases c^α from the remaining equations. However, we have now r -independent Eq. (3.1)₁ for $n > r$ unknowns c^α . Hence, *when the number of phases is greater than the number of components, the equilibrium amount of phases can not be determined uniquely—equilibrium amounts of v phases can be arbitrary, independently of the chemical composition of an alloy element.*

The above conclusions constitute the generalization of the well-known Duhem theorem of classical thermodynamics [13]. It should be once more emphasized, that these conclusions may not be valid if any of the assemblage tensors discussed in Sect. 3.2 would be different from Eq. (3.21) and be c^α -dependent. In that case, it is quite probable, that equilibrium conditions will be sufficient to determine all $n(r+1)$ variables x_K^α, c^α .

When an alloy element contains a phase that does not satisfy equilibrium conditions, it can be said to be in metastable or constrained equilibrium with respect to the flow of matter. The typical examples are diffusionless martensitic phase for which $x_K^\alpha = C_K$ ($\alpha = 1$ – parent phase, $\alpha = 2$ – martensite, $K = 1, \dots, r$).

Let us finally note, that the number of fixed parameters ϵ_α^e, T , is greater than the number of phases. Therefore, any generalization of the well-known Gibb's phase rule must lead to the conclusion that the number of solid phases in a metallic element is unlimited.

3.6. Rate of dissipation. Equation for temperature

Consider the first law of thermodynamics that, for the alloy element under constrained equilibrium, can be written as follows:

$$(3.45) \quad \dot{u} = \dot{q} + \dot{W}, \quad \dot{W} = \tau \cdot \dot{\epsilon},$$

where \dot{q} is the rate of heat supply per unit of mass by an ideal surrounding. Taking into account that $\phi = u - T\bar{s}$, and combining Eqs. (3.45) with Eq. (3.24), one obtains the following form for the entropy production in the course of process connecting the constrained equilibrium states,

$$(3.46) \quad \dot{s} - \frac{\dot{q}}{T} = \frac{1}{T} \dot{D} = (\dot{W} - \dot{W}^{(0)})/T,$$

where \dot{D} is the rate of energy dissipation that can not be negative

$$(3.47) \quad \dot{D} = \sum_{\alpha=1}^n \left[c^\alpha \tau_\alpha \cdot \dot{\epsilon}_\alpha^{pf} - \dot{f}^\alpha c^\alpha - \sum_{K=1}^r \dot{f}_K^\alpha x_K^\alpha \right] \geq 0$$

on account of the second law of thermodynamics. Here we have again introduced the undetermined Lagrange's multipliers Λ^α and Λ_K in order that the corresponding affinities $-\dot{f}^\alpha$ and $-\dot{f}_K^\alpha$ could be regarded as independent. Their connections to ϕ^α is given by Eqs. (3.25)_{3,4}. The multipliers Λ^α and Λ_K can be regarded as dissipationless thermodynamical forces since

$$(3.48) \quad \sum_{\alpha, K}^{n, r} [\Lambda_K (x_K^\alpha c^\alpha + \dot{x}_K^\alpha c^\alpha) + \Lambda^\alpha \dot{x}_K^\alpha] = 0$$

on account of rate constraint relations (cf. Eq. (3.1)₂)

Combining Eqs. (3.46)₁ – (3.47) with Eq. (3.36) one obtains the rate equation for the temperature. It can be written in the form

$$(3.49) \quad c_e \dot{T} = \dot{q} + \dot{Q}_e + \dot{Q}_f + \dot{D}_m + \dot{D}_f,$$

where

$$(3.50) \quad \dot{Q}_e \equiv -T \sum_{\alpha=1}^n c^\alpha \beta_\alpha \cdot (\dot{\epsilon} - \dot{\epsilon}_\alpha^{pf}), \quad \dot{Q}_f \equiv -T \left[\sum_{\alpha=1}^n s^\alpha \dot{c}^\alpha + \sum_{\alpha, K}^{n, r} c^\alpha s_K^\alpha \dot{x}_K^\alpha \right],$$

$$(3.51) \quad \dot{D}_m \equiv \sum_{\alpha=1}^n c^\alpha \tau_\alpha \cdot \dot{\epsilon}_\alpha^{pf}, \quad -\dot{D}_f \equiv \sum_{\alpha} [c^\alpha \phi^\alpha + \sum_{K=1}^n c^\alpha f_K^\alpha \dot{x}_K^\alpha].$$

Here \dot{Q}_e and \dot{Q}_f represent the overall reversible heat of internal elastic straining of all phases and reversible heat of formations of the phases, respectively, whereas \dot{D}_m is the overall mechanical work dissipation, and \dot{D}_f is the irreversible heat of formation of the phases.

Combining \dot{Q}_f and \dot{D}_f one gets the net rate of latent heat of phase formation

$$(3.52) \quad \dot{D}_f + \dot{Q}_f = - \sum_{\alpha=1}^n (u^\alpha \dot{c}^\alpha + c^\alpha \dot{u}^\alpha),$$

where

$$(3.53) \quad \dot{u}^\alpha \equiv \sum_{K=1}^r \frac{\partial u^\alpha}{\partial x_K^\alpha} \dot{x}_K^\alpha$$

and u^α is defined by Eq. (2.32).

It is perhaps worthwhile to emphasize, that the heat of entropy of mixing does not enter Eq. (3.49) since u^α is independent of s^α (cf. Eq. (2.32)). It exemplifies the fact that any configurational entropy (i.e., free energy term that is the linear function of temperature with coefficients depending only on metallography parameters) has no influence on the temperature changes of the system.

3.7. Equations of internal flows – kinetic relations

i) Equations for entropy productions (3.46) – (3.47) immediately suggest a reasonable choice of the set irreversible forces

$$(3.54) \quad Y = \{ \tau_\alpha, -\dot{f}^\alpha, -\dot{f}_K^\alpha \},$$

where the affinities \dot{f}^α and \dot{f}_K^α (defined by Eq. (3.25)_{2,3}) depend on the undetermined Lagrange multipliers that have to be calculated with the aid of the rate constraint relations (3.1)₂. The affinities \dot{f}_K^α can also be expressed in terms of generalized chemical potentials (see Sect. 3.5)

$$(3.55) \quad \dot{f}_K^\alpha = c^\alpha \bar{\mu}_K^\alpha + \bar{A}^\alpha + A_K c^\alpha,$$

where \bar{A}^α are other dissipationless Lagrange multipliers.

The thermodynamic rates associated with the irreversible forces (3.54) are

$$(3.56) \quad \dot{y} = \{ \dot{\epsilon}_\alpha^{\text{pf}}, \dot{c}^\alpha, \dot{x}_K^\alpha \}.$$

To complete the set of all constitutive equations that would enable to describe the evolution of all constrained state variables, when $\epsilon(t)$ and $T(t)$ are prescribed, one needs $6 \cdot n + n(r + 1)$ relationships between irreversible forces (3.54) and thermodynamical rates (3.56). They will be referred to as the *kinetic relations*.

The kinetic relations couple the kinetic equations of formal theory of phase transformations (cf., e.g., [5]) with the rate equations of the intrinsic plastic flow. The cross-effects will be termed “transformation induced intrinsic plasticity” and “strain induced transformations”, where the latter can usually be detected under large plastic deformations of some alloys. The available experimental data concern mainly simple uniaxial stress states and still much of experimental work has to be done (at the border of mechanics and metallography) to deduce meaningful kinetic relations. Here we shall try provisionally to formulate them in a general “mixed” form to encompass preliminary proposals of some researches ([11, 16, 17, 24, 30, 31]). The formulation concerns only monotone phase transformations of the diffusional type.

The generalized internal plastic flow rule at the presence of solid phase transformations can be written in the form

$$(3.57) \quad \dot{\epsilon}_\alpha^{\text{pf}} = \dot{\epsilon}_\alpha^{\text{p}} + \dot{\epsilon}_\alpha^{\text{ip}},$$

where $\dot{\epsilon}_\alpha^{\text{p}}$ represents the usual plastic flow within the whole colony of the phase α . In the first instant this flow will be regarded to be rate-independent and ideal-plastic. In general $\dot{\epsilon}_\alpha^{\text{p}}$ could depend on all intrinsic stresses τ_β ($\beta = 1, \dots, \alpha \dots n$) present in all phases. To simplify the issue we assume that the yield condition of the phase α depends merely on intrinsic stress τ_α acting

in this phase. Thus, we neglect all possible couplings between rate-independent ideal plastic flows in different phases. Let

$$(3.58) \quad F^\alpha(\tau_\alpha, st) = 1, \quad st = \{T, c^\beta, x_K^\alpha\}, \quad \beta = 1, \dots, \alpha, \dots, n, \quad K = 1, \dots, r$$

be the yield condition of the phase α , where the yield function F^α can be scaled so that it is homogeneous of order one, and $F^\alpha(0, st) < 1$. Here we have restricted the dependence of F^α on state variables to the independent variables indicated in the "st". Whenever $F^\alpha < 1$, the local plastic strain must vanish $\dot{\epsilon}_\alpha^p = 0$, and when τ_α and "st" are such that $F^\alpha = 1$, the local ideal plastic flow rule has the classical form

$$(3.59) \quad \dot{\epsilon}_\alpha^p = \langle \lambda^\alpha \rangle \mathbf{F}^\alpha, \quad \mathbf{F}^\alpha \equiv \frac{\partial F^\alpha}{\partial \tau^\alpha},$$

where the symbol $\langle \cdot \rangle$ denotes the Macauley function, $\langle z \rangle = z$ when $z > 0$ and $\langle z \rangle = 0$ otherwise. The undetermined multiplier λ^α must be non-negative to satisfy Eq. (3.47) when all $\dot{c}^\alpha = 0$ and $\dot{x}_K^\beta = 0$ ($\beta = 1, \dots, \alpha, \dots, n$). It should be determined with the aid of local consistency relation $\dot{F}^\alpha = 0$.

The second tensor $\dot{\epsilon}_\alpha^{ip}$ occurring in Eq. (3.57) describes *thermodynamic cross effect-transformation induced intrinsic plasticity*. To encompass the frequent practice we shall express it in terms of \dot{c}^α and \dot{x}_K^α (instead of \dot{f}^α and \dot{f}_K^α) assuming, in the first instant, that the relationship is linear

$$(3.60) \quad \dot{\epsilon}_\alpha^{ip} = \sum_{\beta=1}^n \left[\mathbf{l}_{\alpha\beta}^\beta \dot{c}^\beta + \sum_{K=1}^r \mathbf{l}_{\alpha\beta}^K \dot{x}_K^\beta \right].$$

In general $\mathbf{l}_{\alpha\beta}^\beta$ and $\mathbf{l}_{\alpha\beta}^K$ can be functions of all state variables.

The kinetic equations of internal flow of matter within the multiphase element we adopt in the form

$$(3.61) \quad \begin{aligned} \dot{c}^\alpha &= \sum_{\beta=1}^n \left[X_{\beta}^\alpha \dot{f}^\beta + \sum_{K=1}^r (X_{\beta}^{\alpha K} \dot{f}_K^\beta) + \lambda^\beta \mathbf{X}_{\alpha\beta} \cdot \mathbf{F}^\beta \right], \\ \dot{x}_J^\alpha &= \sum_{\beta=1}^n \left[\left(\sum_{K=1}^r X_{J\beta}^{\alpha K} \dot{f}_K^\beta \right) + X_{J\beta}^\alpha \dot{f}^\beta + \lambda^\beta \mathbf{X}^{\alpha\beta} \cdot \mathbf{F}^\beta \right]. \end{aligned}$$

The first two terms occurring in Eqs. (3.61) represent kinetic law of phase transformations. The last terms describe the possible other thermodynamic effect-strain induced phase transformations. The phenomenological functions occurring in Eqs. (3.61) should be deduced from available experimental data concerning these phenomena what is still a labour task that requires separate treatment. To this end the results of so-called formal theory

of phase transformations (CHRISTIAN [5]) may be used. Since the strain-induced phase transformations are usually detected at large overall plastic deformations, we shall further assume that $X_{\alpha\beta} \approx 0$, $X_j^{\alpha\beta} = 0$.

ii) For fixed state one can, at least formally, determine c^α and x_j^α from Eqs. (3.61) and $\dot{\varepsilon}_\alpha^{ip}$ from Eq. (3.60). Suppose that overall strain rate $\dot{\varepsilon}$ and temperature rate \dot{T} are prescribed. To find the explicit relation between $\dot{\varepsilon}_\alpha^{ip}$ and $(\dot{\varepsilon}, \dot{T})$ substitute Eqs. (3.32)₁, (3.59) into the local consistency equation $\dot{F}^\alpha = 0$ ($F^\alpha = 1$) and solve the obtained equation with respect to λ^α . The eventual result is ($F^\alpha = 1$)

$$(3.62) \quad H^\alpha \lambda^\alpha = \langle F^\alpha \cdot L_\alpha \dot{\varepsilon} + (F_T^\alpha - F^\alpha \cdot \beta_\alpha) \dot{T} - F^\alpha \cdot L_\alpha \dot{\varepsilon}_\alpha^{ip} + \sum_{K=1}^r (\tau_K^\alpha \cdot F^\alpha + F_K^\alpha) x_K^\alpha + \sum_{\beta=1}^n F_\beta^\alpha c^\beta \rangle,$$

where

$$(3.63) \quad H^\alpha = F^\alpha \cdot L_\alpha F^\alpha > 0, \quad F_\beta^\alpha \equiv \frac{\partial F^\alpha}{\partial c^\beta}, \quad F_T^\alpha \equiv \frac{\partial F^\alpha}{\partial T}, \quad F_K^\alpha = \frac{\partial F^\alpha}{\partial x_K^\alpha}.$$

Using Eq. (3.62) one can at each step calculate $\dot{\varepsilon}^p$, $\dot{\varepsilon}^{pi}$, $\dot{\tau}^\alpha$, \dot{q} and overall stress-rate $\dot{\tau}$ through Eqs. (3.59), (3.57), (3.33), (3.49) and (3.34), respectively. The set of rate equations for all variables is completed. When \dot{q} instead of \dot{T} is prescribed or when additionally strain-induced plasticity effect should be included, ($X_{\alpha\beta} \neq 0$ or/and $X_j^{\alpha\beta} \neq 0$), the procedure of calculation of λ^α must be repeated in the similar manner as it was done above. However, the application of the presented thermodynamical reference model requires careful estimation of the initial value of intrinsic stress, say $\tau_{(i)}^0$, that develop in the new phase (say $\alpha = (i)$) at the very beginning of its formation, (say at time $t = t_i^0$ when $c^{(i)} \approx 0$) from the parent phase $\alpha = (i-1)$. This stress does not need to coincide neither with the instantaneous overall stress $\tau(t_i^0)$ nor with the instantaneous intrinsic stress of the parent phase $\tau_{(i-1)}(t_i^0)$. Equivalently one can try to estimate the initial "phase distortion" of the new phase. Its connection to $\tau_{(i)}^0$ is

$$(3.64) \quad \varepsilon_{(i)}^{ip}(t_i^0) - \left[\mathbf{M} \left(\sum_{\alpha=1}^{i-1} c^\alpha L_\alpha \varepsilon_\alpha^{pf} \right) \right]_{t=t_i^0} = \mathbf{M}(t_i^0) \tau(t_i^0) - \mathbf{M}_{(i)}(t_i^0) \tau_{(i)}^0 + [T(t_i^0) - T_0] [\bar{\alpha}(t_i^0) - \bar{\alpha}_{(i)}(t_i^0)]$$

on account of Eq. (3.32). The left-hand side of Eq. (3.64) represents the extra distortion of the new phase measured with respect to inelastic strain of the macro-element at early stage of nucleation of the phase. For ideal-plastic phases the initial value of usual plastic strain in the phase (i) may be assumed to be negligible ($\varepsilon_{(i)}^p(t_i^0) = 0$). Any choice of $\tau_{(i)}^0$ or extra stress, $\Delta\tau_{(i)} = \tau_{(i-1)}(t_i^0) - \tau_{(i)}^0$

constitutes significant hypothesis which can be verified, for instance, by trial and error when comparing the experimental data with the theoretical one.

3.8. On overall transformation induced plasticity

A part of overall inelastic strain rate $\dot{\boldsymbol{\varepsilon}}^{\text{pf}}$ which represents the overall transformation plasticity effect may be defined as (see Eq. (3.37))

$$\dot{\boldsymbol{\varepsilon}}_{\text{tp}} \equiv \dot{\boldsymbol{\varepsilon}}^{\text{pf}} - \dot{\boldsymbol{\varepsilon}}^{\text{p}}, \quad \dot{\boldsymbol{\varepsilon}}^{\text{p}} = \dot{\boldsymbol{\varepsilon}}^{\text{pf}} \Big|_{\dot{b}_{\mathbf{k}}^{\text{p}} = 0} = \mathbf{M} \left(\sum_{\alpha=1}^n c^{\alpha} \mathbf{L}_{\alpha} \dot{\boldsymbol{\varepsilon}}_{\alpha}^{\text{p}} \right) \Big|_{\dot{b}_{\mathbf{k}}^{\text{p}} = 0},$$

where $\dot{\boldsymbol{\varepsilon}}^{\text{p}}$ is the virtual thermo-plastic strain rate that would have occurred had the phase transformation process been instantaneously stopped. The peculiarity of $\dot{\boldsymbol{\varepsilon}}_{\text{tp}}$ is that its deviatoric part being negligible for $\tau = 0$ becomes significant for some non-zero stresses that are much smaller than the yield limit of weakest phase (cf., e.g., GAUTIER *et al.* [25]). Therefore, the spherical part of $\dot{\boldsymbol{\varepsilon}}_{\text{tp}}$ is sometimes termed “metallurgical” strain rate ([30, 31] to emphasize the fact that this part is not representative for experimentally observed transformation plasticity effect.

Consider 3-axial resemblance of typical uniaxial experimental program concerning isothermal ($T = T_0$) decomposition of parent phase ($\alpha = 1$) into new harder phase ($\alpha = 2$) under constant overall stress $\tau = \tau_*$ (so-called static conditions) applied before the beginning of the transformation, say at time $t < t_2^0$, where t_2^0 is the time when transformation starts. Assume that yield functions $F^{(\alpha)}$ are independent of c^{α} and $x_{\mathbf{k}}^{\alpha}$, and that all phases have common elastic moduli. Moreover, applied stress τ_* is small such that $F^{(1)}(\tau_*) < 1$ and $F^{(2)}(\tau_*) < 1$. Let the initial intrinsic stress in the new phase be $\tau_{(2)}(t_2^0) = \tau_* - \Delta\tau_*$, what implies that the initial phase distortion (cf. Eq. (3.64)) is

$$(3.65) \quad \boldsymbol{\varepsilon}_{(2)}^{\text{e}}(t_2^0) = \mathbf{M} \Delta\tau_*$$

since $\boldsymbol{\varepsilon}_{(1)}^{\text{pf}}$ vanishes for $t < t_2^0$. After completion of the phase transformation, say at time t_2^{∞} , $c^{(2)} = 1$, and elastic strain of the new phase $\boldsymbol{\varepsilon}_{(2)}^{\text{e}}(t_2^{\infty})$ must be the same as elastic strain of the parent phase $\boldsymbol{\varepsilon}_{(1)}^{\text{e}}(t_2^0) = \mathbf{M}\tau_*$ before transformation because of the elastic moduli of both phases coincide. Hence, the total strain “amplitude” $\Delta\boldsymbol{\varepsilon}_{\text{tp}}$, total heat absorbed by an environment ΔQ , and the total energy dissipation ΔD due to phase transformation are, respectively,

$$\begin{aligned}
 \Delta \varepsilon_{ip} &= \varepsilon(t_2^\infty) - \mathbf{M} \tau_* = \mathbf{M} \Delta \tau_* + \Delta \varepsilon_{(2)}^p; & \Delta \varepsilon_{(2)}^p &= \int_{t_2^0}^{t_2^\infty} \dot{\varepsilon}_{(2)}^p dt, \\
 (3.66) \quad \Delta Q &= \tau_* \cdot \Delta \varepsilon_{ip} - \tau_* \cdot (\bar{\alpha}_{(2)} - \bar{\alpha}_{(1)}) T_0 + \bar{u}_{(1)}^* - \bar{u}_{(2)}^*, \\
 \Delta D &= \tau_* \cdot \Delta \varepsilon_{ip} - (\varphi_*^{(2)} - \varphi_*^{(1)}) \geq 0
 \end{aligned}$$

provided that no plastic flow occurs in the new phase ($\dot{\varepsilon}_{(2)}^p = 0$). Here, $\varphi_*^{(\alpha)} = \bar{u}_\alpha^* - T_0 \bar{s}^\alpha$ are the free energies of both phases ($\alpha = 1, 2$) at $T = T_0$ and $\varepsilon_{(\alpha)}^e = 0$, and the meaning of other symbols are explained in Sect. 2 (cf. Eq. (2.37)).

It is seen that free energy of macro-element can only decrease when $\tau_* = 0$, and the total work expanded by $\tau_* \neq 0$ during phase transformation need not be positive since, in general, $\varphi_*^{(1)} > \varphi_*^{(2)}$. The possible plastic flow in the parent phase has no influence on final total strain $\Delta \varepsilon_{ip}$. However, it affects $\varepsilon_{ip} - c^{(2)}$ curve at time $t < t_2^\infty$. To discuss this effect assume that \mathbf{M} and $\dot{\varepsilon}_\alpha^p$ ($\alpha = 1, 2$) are isotropic tensors, and $F^{(1)}$ is independent of hydrostatic pressure. Denote by "prime" the deviatoric parts of appropriate tensors, and note that Eqs. (3.32) and (3.65) imply $\tau_{(1)} = \tau'_* + c^{(2)} \Delta \tau'_*$ as long as the weaker phase is deformed elastically. Thus, the plastic flow in the parent phase occurs provided that $F^{(1)}(\tau'_* + \Delta \tau'_*) > 1$. This can be interpreted as "lowering" of the current yield point of metallic element in certain directions. Some experimental observations ([30, 31]) suggest that $\Delta \varepsilon'_{ip}$ is colinear with τ'_* . Therefore, it is expedient to assume linear relation between τ'_* and $\Delta \tau'_*$

$$\Delta \tau'_* = \eta \tau'_*,$$

where η can depend on the initial pressure in the new phase. In this case the critical amount of new phase $c_0^{(2)}$ for which the plastic flow in the parent phase starts is

$$c_0^{(2)} = [1 - F^{(1)}(\tau'_*)] / [\eta F^{(1)}(\tau'_*)]$$

and, it can be shown that the plastic straining is proportional, such that relation between ε'_{ip} and $c^{(2)}$ is

$$\begin{aligned}
 \varepsilon'_{ip} &= \frac{\eta}{2G} m(c^{(2)}) \tau'_*, \\
 m(c^{(2)}) &= \begin{cases} c^{(2)} & \text{when } c^{(2)} < c_0^{(2)}, \\ 1 - c_0^{(2)}(1 - c^{(2)})/c^{(2)} & \text{otherwise,} \end{cases}
 \end{aligned}$$

where G is the elastic shear modulus.

This qualitatively agrees with that what is observed during uniaxial tension tests. The normalized function m for different c_0 is shown in Fig. 3. The thick solid line shown in this figure represent the experimental data collected by LEBLOND *et al.* [30, 31] for the bainitic transformation in A.533 steel. The discrepancy seems to be acceptable for $c_0^{(2)} \approx 0.15$. Using GREENWOOD—JOHNSON formula [6] for total strain amplitude, the parameter η can be expressed in terms of yield limit Y at simple tension of weaker phase (parent phase) and the volume dilatation $\Delta V/V$ associated with the phase transition, $\eta = 5G\Delta V/(2YV)$. For austenite-pearlite transformation $\Delta V/V = 3.6 \cdot 10^{-3}$ (GAUTIER *et al.*, 1987). Taking $G/Y = 600$, one gets $\eta = 5.4$. Hence, plastic flow in austenite occurs when $F_* > 0.16$. The average stress deviator in the pearlite colony at the early stage of transition is $\tau'_{(2)}(t_2^0) = -4.4\tau'_*$. At the termination of the phase transition it relaxes to τ'_* .

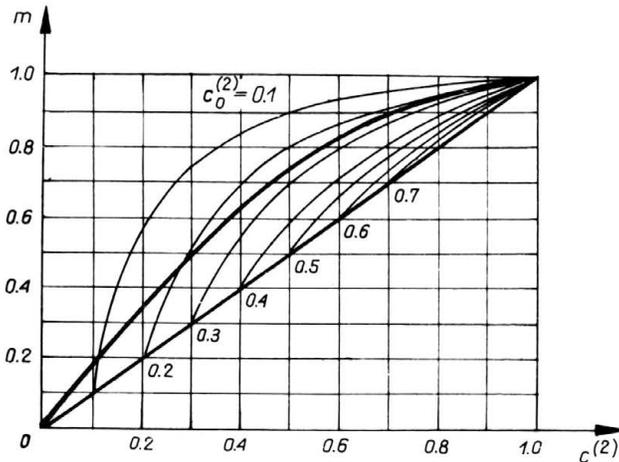


FIG. 3.

4. Discussion

Application of method of thermodynamics when modelling the behaviour of elastic-plastic alloys under ongoing solid-solid phase transformations requires use of a concept that links the external state variable (overall strain or overall stress) with intrinsic deformation-type variables or intrinsic force-type variables. Six simple assemblage relations (3.21) adopted in this paper connect overall strain with intrinsic elastic strains of individual phases. This enables to estimate the evolution of mean stresses acting over the colony of individual phases — the factor that seems instrumental in explanation of TRIP. However, the instantaneous intrinsic stress levels depend on the initial stress acting in the

new phase at the beginning of its formation. The required implicit relation, between extra stress $\Delta\tau_{(i)} = \tau_{(i-1)}(t_i^0) - \tau_i^0$ (cf. Sect. 3.7) in the new phase, and intrinsic stress in parent phase $\tau_{(i-1)}(t_i^0)$, at the beginning of nucleation of new phase, constitutes inherent part of the presented reference model, and it does not belong to the group of thermodynamical equations of internal flows. In fact, this relation should represent specific micro-physical mechanism of formation of new phase in stressed environment. The evolution of the extra stress when phase transformation proceeds depend much on the specific form of kinetic laws (3.62) for $\dot{\varepsilon}_{\alpha}^p$, and when no plastic flow in the parent and new phases occur and group of phenomenological tensors $\mathbb{I}_{\beta}^{\alpha}$ is skewsymmetric ($\mathbb{I}_{\beta}^{\alpha} = -\mathbb{I}_{\alpha}^{\beta}$) then extra-stress is kept approximately constant provided that $\mathbb{I}_{\alpha\beta}^k = 0$. This specific case should be carefully investigated in further studies. Tensors $\mathbb{I}_{\beta}^{\alpha}$ can possibly depend also on $\tau_{(i-1)}(t_i^0)$. It is shown in this paper that even if effect of transformation induced intrinsic plasticity is neglected, the presented model predicts the accumulation of total strain in a way that qualitatively agrees with observations made during uniaxial experiments. It is perhaps worthwhile to emphasize that the presented framework includes in the limit, when elastic strains in all phases vanish, thermodynamics of solid solutions that constitutes the theoretical background for constructions of well-known equilibrium diagrams. It is believed that the presented general framework will help to systematize research in metallo-thermo-mechanics. Implication of inequality (3.47) should be investigated after specification of all constitutive tensors in every individual situation. The important factors that should be accounted for in further generalization of the model are:

Strain hardening. This requires, among others, specifications of the stored internal energy u_{α}^* and stored entropy s_{α}^* in terms of the appropriate internal variables describing the hardening. The constitutive equations of mechanical behavior that account for the isotropic hardening and accord with the present theoretical framework under assumption (3.6) and $\mathbb{I}_{\alpha\beta}^k = 0$, may be found in RANIECKI [23].

Strain-rate effects. Here one can attempt to cast recent achievements in formulation of unified creep-plasticity models (cf., e.g., KRIEG *et al.* [28], KORHONEN *et al.* [27]).

Other metallographic parameters, e.g., mean grain sizes of individual phases.

Thermodynamics of continuous solids whose "physical point" is elementary system discussed here, can be developed by using appropriate balance laws and the classical principle of local state.

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